# 2009 DOE Hydrogen Program High Temperature Thermoelectric Materials

Norbert B. Elsner Hi-Z Technology March 20, 2009

Project ID # acep 04 elsner

### Overview

### Timeline

Project start date: 28, June 2006
Project end date: 7 August 2009

Percent complete: 77%

### **Barriers**

•Develop low contact resistance for production scale into Quantum Well materials

•Develop better technique for appraising microstructure and measuring the figure of Merit (ZT)

•Obtain outside confirming thermoelectric measurements

### **Budget**

Total project funding

DOE share: 850,000

Contractor share: 298,000BAE Systems

Funding received in FY08 : 375,000

• Funding for FY09: 375,000

### **Partners**

•SUNY Albany nanostructure group

•General Atomics nano film production facility

•UCSD for thermal conductivity

measurements

BAE Systems

### Objectives

- Obtain Thermoelectric properties measurements outside Hi-Z on Quantum Well materials that exhibit high figures of merit (ZT)
- Develop new techniques for obtaining ZT directly
- 3. Develop techniques for obtaining low contact resistance joints
- 4. Optimize the sputter deposition techniques for producing consistent material and how they can be scaled up.
- 5. Develop low thermal conductivity substrate materials.

### **APPROACH**

# Criteria/Components for Developing QW Films

#### 1. QW films

- Compositions defined: N and P Si/SiGe, P type B<sub>4</sub>C/B<sub>9</sub>C and N and P type Si/SiC
- Deposition parameters established with sputtering
- Third party verification of QW films performed and continuing

#### 2. Substrate

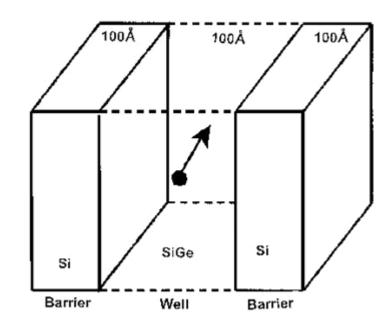
- Need low thermal K materials at low cost and can be readily coated with QW films
- 3. Joining techniques needed for fabricating couples that will operate at various  $T_{\rm H}$  up to 1000°C
- 4. Life testing of materials and couples
  - Isothermal
  - Gradient
- 5. Fabricate and evaluate modules and production scale up.
- 6. Continue cost analysis as fabrication techniques evolve

### Relevance

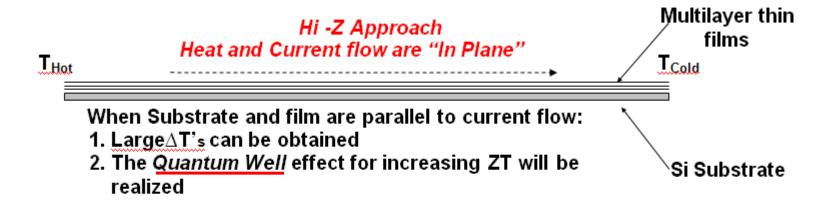
- •Projected increase from the current 5% to 15- 40% efficiency
- Waste heat can be recovered from any vehicle, industrial and geothermal heat sources
- •Hi-Z pursuing nanosized Quantum Well materials Their potential for high ZTs (figures of merit) which means higher efficiencies.
- •Many samples prepared with high Seebeck coefficients ( $\alpha$ 1,000 Micro V/°C) and low electrical resistivities ( $\rho$ 1milli  $\Omega$  –cm)
- •Several measurements by outsiders confirm Hi-Z's encouraging results for  $\alpha, \rho$ , and  $\kappa$
- •New measuring technique developed for measuring ZT directly.
- •Hi-Z is pursuing fabrication/testing of N&P couples and modules
- •Over eight—1 Billion sized markets exist for converting waste heat into electricity if more efficient thermoelectrics can be developed.

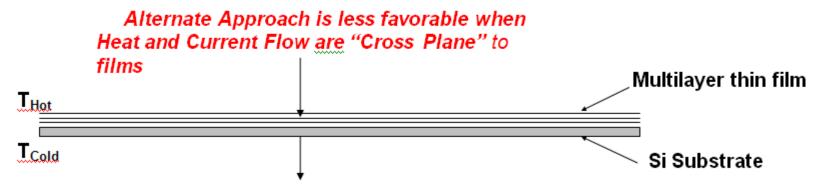
### Two-Dimensional Enhanced Thin Film Thermoelectrics using Quantum Well Structures

- Active layer sandwiched between materials with band offset to form a barrier for the charge carriers
- Increased Seebeck coefficient (α) due to an increase in the density of states
- Significant reduction on resistivity (ρ) due to quantum confinement of carriers
- Significant reduction on thermal conductivity (κ) due to strained lattice and other factors
- Quantum Well (QW) effects become significant at a layer thickness of <200Å</li>



### Enhanced Thin Film - Orientation Difference

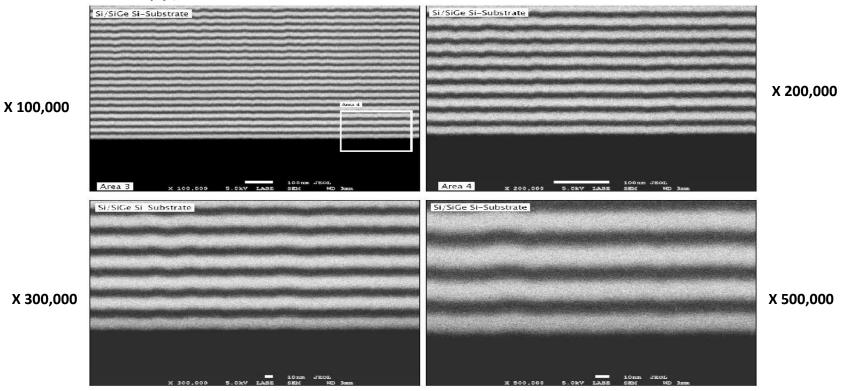




- Large \( \Delta \text{T's are difficult to obtain across the thin films. Large heat fluxes required
- 2. Not useful for power generator
- 3. No Quantum Well effect is realized
- 4. However thermal conductivity will be reduced.

### Si/SiGe Films on Cross-section

Films were sectioned and then viewed by SEM (scanning electron microscopy)

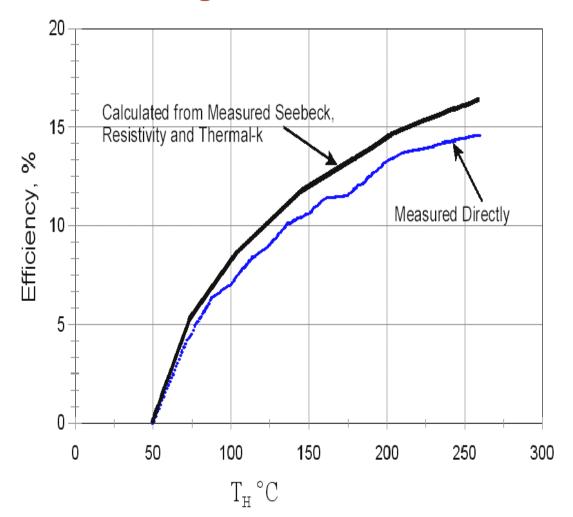


Slight waving of layers is caused at the interfaces to the large difference between the atom size of a Si and a Ge



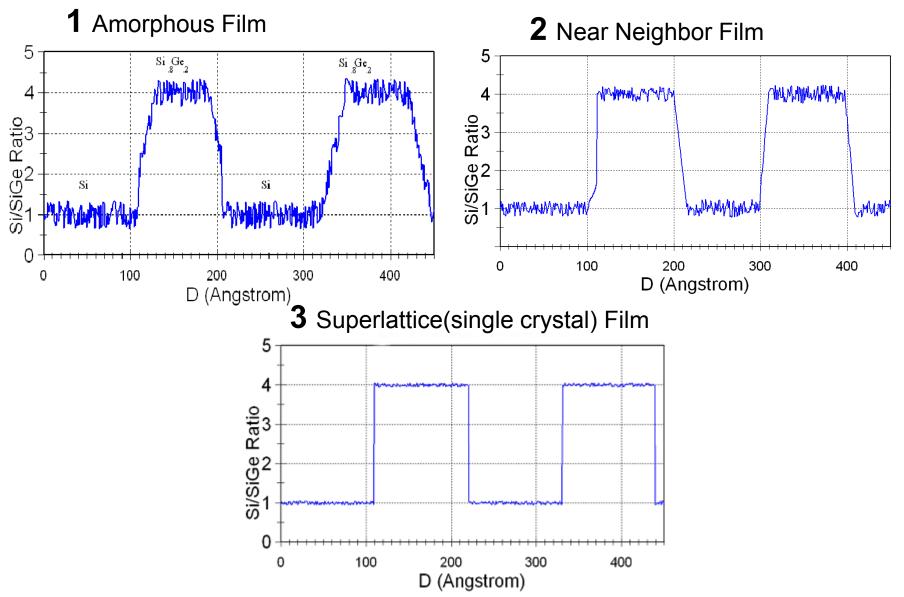
### Quantum Well Couple Efficiency

### **Highest Measured Thermoelectric Efficiency**

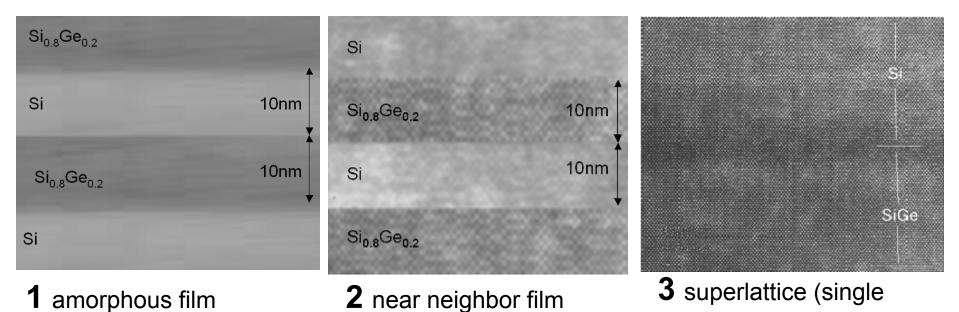


- Measured Quantum
   Well Couple Efficiency
   Versus temperature at
   a T<sub>C</sub> = 70°C
- Over 100 Data Points
   Were Obtained N-leg
   Si/SiGe, P-leg B<sub>4</sub>C/B<sub>9</sub>C
- Both Films 11 μm Thick and Deposited on a 5 μm Thick Si Substrate
- Average ZT for N &P couple is ~ 3

### Auger Electron Spectroscopy (AES) Results



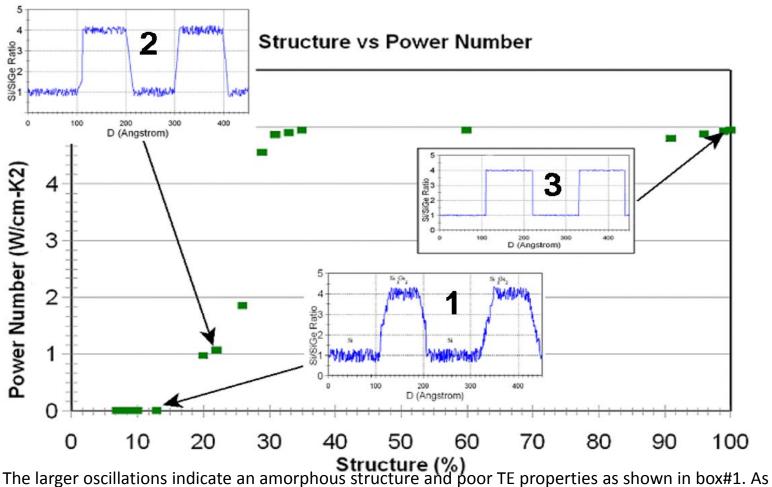
#### Transmission Electron Microscopy (TEM) Results



- Each layer is ~10nm thick
  - •The boundaries between each layer are as sharp as the as fabricated films indicating no diffusion is occurring and films do not break up

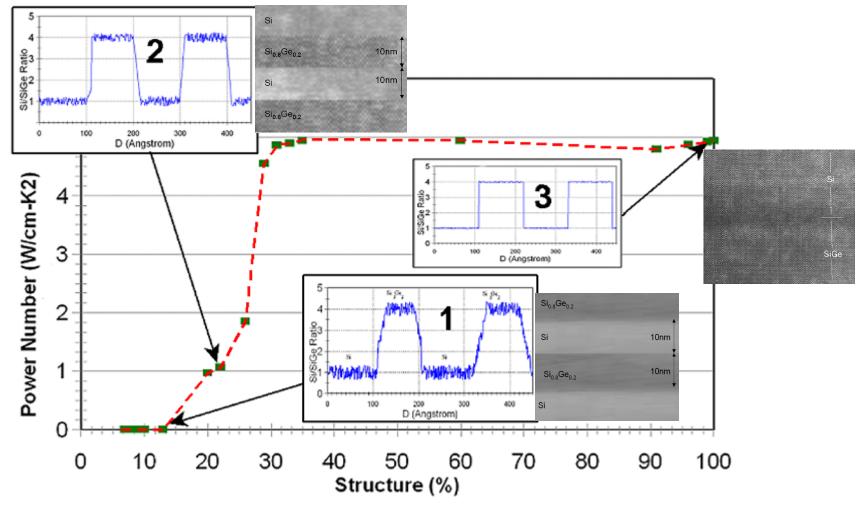
crystal) film

# Relation between TE properties and structure using AES



The larger oscillations indicate an amorphous structure and poor TE properties as shown in box#1. As oscillations variance decrease as shown in box#2 TE properties begin to improve. When best TE properties are obtained the profile in box#3 is obtained.

# Relation between TE properties and structure using AES & TEM

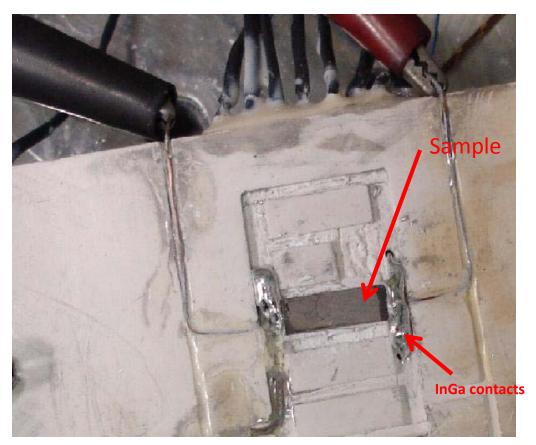


The larger oscillations indicate an amorphous structure and poor TE properties as shown in box#1. As oscillations variance decrease as shown in box#2 TE properties begin to improve. When best TE properties are obtained the profile in box#3 is obtained. For superlattice (box#3) structures is ~100%, for near neighbor (box#2) structures is ~ 10-90%, and for all amorphous (box#1) structure ~0%

# Thermelectric Property Measurements with Boron Nitride Test Fixture

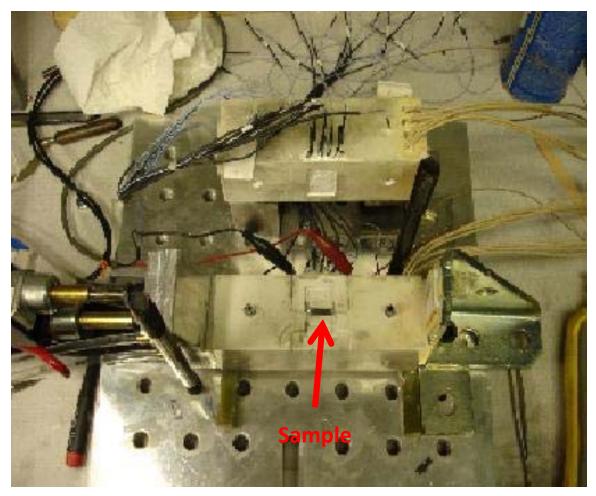
Goal: Obtain ZT and efficiency directly

- •Si/SiGe Films deposited on Si Substrate
- •Sample housed in large two large blocks of BN
- ΔT imposed on sample is the same as measured in BN
- •Heat flowing through QW films is readily calculated using a conservative thermal conductivity
- Both Seebeck coefficient and electrical resistivity measured (p)
- •From these measurements an approximate efficiency and ZT obtained



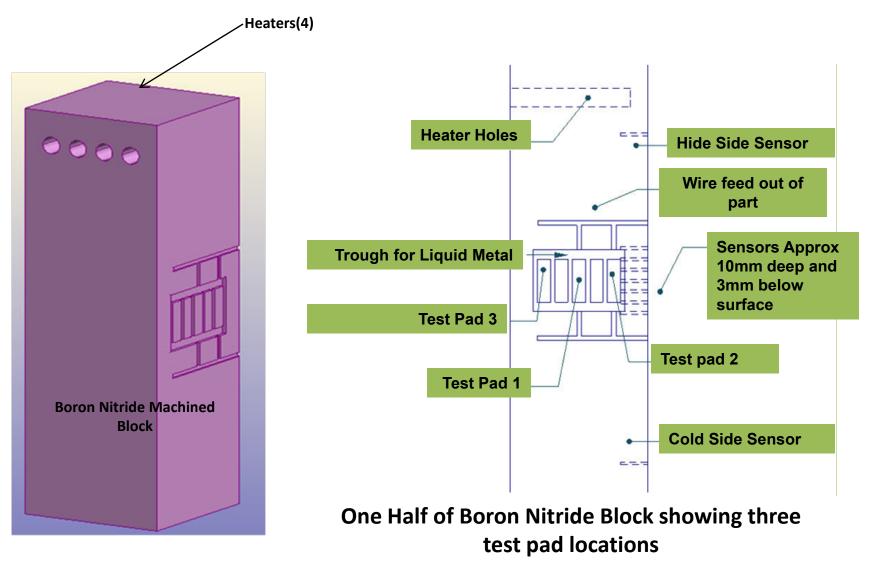
Sample Position in BN Test Fixture. Up to 5 samples can be evaluated at once. Liquid InGa is used to contact the sample.

# Thermal Properties Measurements Boron Nitride Test Fixture



Both Halves of the BN Test Fixture are Shown with Test Sample in Place

# Thermal Properties Measurements with Boron Nitride Test Fixture



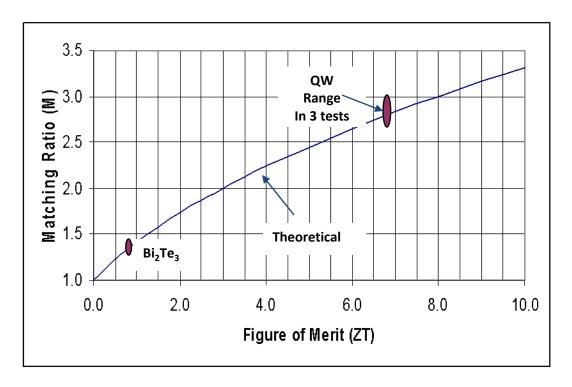
# Summary of QW Film Data Obtained With Boron Nitride Test Fixture

		Temp	eratures	Measuremer	nts	Lit. Data	Efficiency Based on ZT from Measured Da Bulk κ				nd Literature	Normalized Efficiency to Bi <sub>2</sub> Te <sub>3</sub> & $\Delta T$	
	Sample #	T <sub>H</sub> (°C) (	$T_{C}$ $\Delta T$ $^{\circ}C)$ $(^{\circ}C)$	$\begin{array}{ccc} \alpha & \rho \\ (\mu V)^{\circ} & (m\Omega \\ C) & \text{-cm}) \end{array}$	P Pwr (µW)	κ (W/cm -°C)	Z (1/K)	$ZT_{ave}$	М	Carnot Efficienc y (%)	Materials Efficiency( a) η <sub>mat</sub> (%)	Total Efficiency (%)	
	Bi <sub>2</sub> Te <sub>3</sub>	74.6 6	5.08 9.52	-176.7 1.02	7.35	0.012	0.002	~0.8	1.3	2.74	15.6	0.43	1.00
	HZ-069	77.6 7	0.49 7.10	794.6 0.28	0.58	0.110	0.020	~7	2.8	2.03	48.6	0.98	3.11
Si/SiGe -	HZ-071			758.8 0.25		0.110	0.021	~7	2.9	2.04	49.4	1.01	3.17
Į	HZ- 040108	83.07 7	72.1 = 10.9	642.7 0.22	1.9	0.110	0.016	~6	2.6	3.08	45.2	1.39	2.90
	Efficiency based on measured power and heat balance												
	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$				iciency	Good correlation between both							
	[	Bi <sub>2</sub> Te <sub>3</sub> HZ-069	520.9 65.5	-3.67 -0.29		159 : 21 :	1670 86		0.4 0.6	<b></b>	1.00 2.06	appro	oaches
9	Si/SiGe	HZ-071 HZ- 040108	175.8 121.1	-0.90 -0.94		45 40	220 160		0.8 1.1		2.39 2.32		
	-	Maximum efficiency calculation for QW from efficiency-current plot  Value at maximum efficiency							fficiency				
		HZ-069 HZ-071	39.29 123.1	-0.10 : -0.44		21 : 45 :	60		0.9		2.96		
Si/	SiGe	HZ- 040108	84.75	-0.44		40 :	125		1.5	<mark></mark>	2.98		

Sample # N type bulk Bi<sub>2</sub>Te<sub>3</sub>

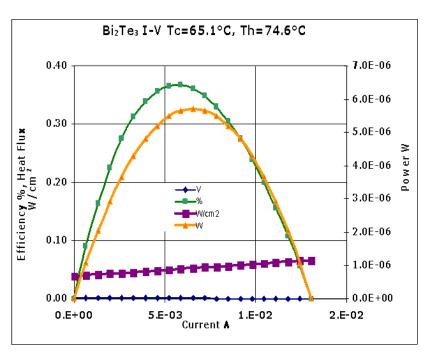
Sample # HZ-069: Hi-Z UCSD sample, P type QW Si/SiGe (50 periods) on Si substrate Sample # HZ-071: Hi-Z JPL sample, P type QW Si/SiGe (50 periods) on Si substrate Sample # HZ-040108: Hi-Z sample, P type QW Si/SiGe (50 periods) on Si substrate

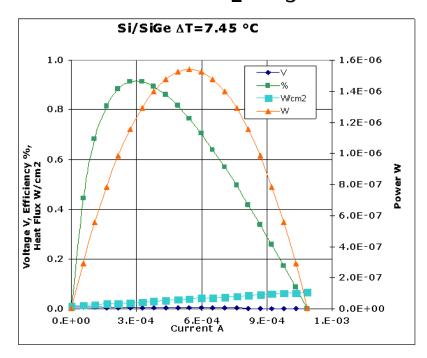
### Theoretical Variation of Resistance Matching Ratio (M) with Figure of Merit (ZT)



Note that the ZT values of the Bi<sub>2</sub>Te<sub>3</sub> alloy and Si/SiGe QW samples are close to the theoretical values.

# QW Performance Curves Based on Boron Nitride Test Data for QW Si/SiGe and bulk type Bi<sub>2</sub>Te <sub>3</sub>





Typical Thermoelectric Performance Curves for Bi<sub>2</sub>Te<sub>3</sub> Based Alloys.

- •Note that the max power and max efficiency values are relatively close with Bi<sub>2</sub>Te<sub>3</sub> where as higher ZT materials show a wider separation as shown in with the Si/SiGe performance curves
- •With Si/SiGe however it has a higher ZT and the max efficiency and max power points as further separated.

# Thermoelectric Property Measurements by Various Organizations

- University of California San Diego (UCSD)
- National Institute of Standards and Tests (NIST)
- Jet Propulsion Laboratory (JPL)
- Hi-Z
- Consultant
- Above organizations have evaluated Hi-Z's QW films.
- All organizations show large gains in thermoelectric properties primarily in Seebeck coefficient.

## Thermoelectric Property Measurements by Various Organizations and Calculated Figures of Merit ZT and Efficiency for Si/SiGe QW Materials

	Measured Seebeck α	Measured electrical resistivity - 2 probe technique (includes contact resistance)	Measured electrical resistivity - 4 probe technique (excludes contact resistance)	Power Factor α <sup>2</sup> /ρ	Figure of Merit <sup>(1)</sup> ZT =	Projected Efficiency <sup>(1)</sup> 50-250°C	Projected Efficiency <sup>(1)</sup> 50-600°C
	μV/°C	mΩ-cm	mΩ-cm	μW/cm°K²	$\alpha^2 x T / (\rho x \kappa)$	%	%
Typical Former QW sample	1100	1		1210	>3	13	23
Cleaned Contacts	1200		0.04	36000		28	41
QW sample data observed by UCSD at Hi-Z (12/06)	1200	0.75		1920	>4	16	30
QW sample data observed by UCSD at Hi-Z (12/06)	1200		0.042	34286	>10	28	40
QW sample data at Hi-Z observed by NIST (3/07)	1302	0.36		4709	>10	17	32
QW sample data at Hi-Z observed by NIST (3/07)	1302		0.05	33904	>10	28	40
QW sample data measured by UCSD at UCSD (12/06)	1000	0.75		1333	>3	14	25
QW sample data measured by UCSD at UCSD (09/07) QW sample data measured by	800 800	0.33	0.2	1939 3200	>4 >8	19 25	32 32
UCSD at UCSD (09/07)	1500		0.12	18750	>10	27	39
QW sample data measured by JPL at JPL (10/07-Interim Preliminary Report)	1420	0.35 <sup>(2)</sup>		Footnote # 4	Footnote # 4	Footnote # 4	Footnote # 4
QW sample data measured by JPL at JPL (10/07-Interim Preliminary Report)	1420		$m\Omega$ – cm range should be <0.35 <sup>(3)</sup>	Footnote # 4	Footnote # 4	Footnote # 4	Footnote #4
Current Bi <sub>2</sub> Te <sub>3</sub> bulk alloy	220	1.1	1.1	44	0.8	5	Properties degrade >300°C

Notes:

Kev:

<sup>(4)</sup> JPL requested that the encouraging calculated Power Factor, ZT and efficiencies not be included in this table until more samples are measured for thermal properties. These additional samples are being prepared and will be measured by all the interested parties to obtain κ and ZT.

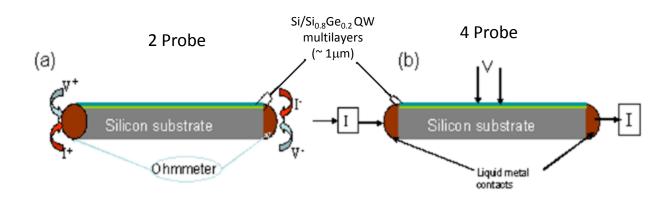
112)		
	Typical former sample	Prior independent measurements at UCSD
	Ion beam cleaning of sample ends followed immediately with InGa	Recent Independent measurements at UCSD & JPL
	Prior Independent UCSD & NIST measurements at Hi-Z	Current commercial materials

All projected Figures of Merit (ZT) and efficiencies (%) are based on measured α and ρ and literature published bulk thermal conductivity, κ = 0.11 W/cm<sup>\*</sup>K (which is conservative).
 κ was not measured by UCSD, NIST, or JPL. Realistic efficiencies include substrate and module structure parasitic heat losses.

<sup>(2)</sup> JPL two probe electrical resistivity based on resistance (9.16Ω) and geometry (1.3cm x 0.5cm x 0.0001cm).

<sup>(3)</sup> JPL four probe electrical resistivity values fluctuated.

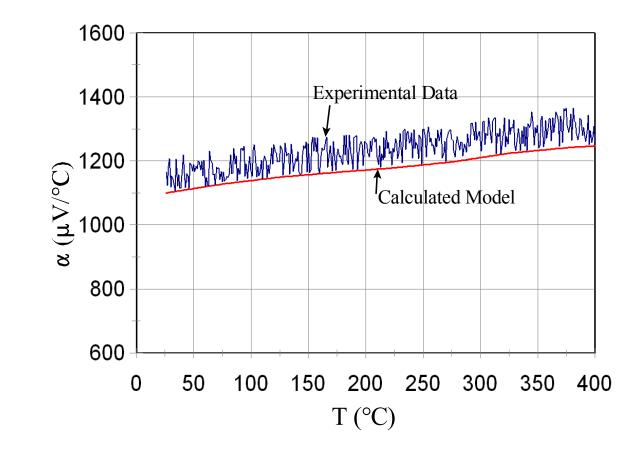
# Schematic of the Measurement Setups for Obtaining the Resistivity (R) of the Si/SiGe Multilayer on Si Substrates



- (a) two-terminal Ohmmeter (Tegam, Inc.) probes and,
- (b) four probe arrangements, where the current is sent through the liquid metal contacts at the ends while the voltage is measured along the sample with two more probes. Note: typical specimen is grown to 8-10  $\mu$ m of Si/SiGe multilayer; however, test specimen had 1  $\mu$ m Si/SiGe

The resistivity parallel to the layers ( $\rho$ ||) is then calculated from measured resistance (R) through the sample geometry. The lateral dimensions of the sample are 1.2 cm x 0.5 cm, and the thickness of the Si/SiGe multilayer are ~1  $\mu$ m (the substrate is ~500  $\mu$ m thick).

## Calculated vs. Experimental Seebeck Coefficient vs. Temperature for QW Films



The calculated model closely matches the experimental data. This excellent match between the analytical and experimental data underscores the model's viability for understanding the  $\alpha$  behavior.

# Measurement of superlattice thermal conductivity (κ) on Hi-Z enhanced films at the University of California San Diego

#### by Dr. Prab Bandura, UCSD

- Measurements on Si<sub>0.8</sub>Ge<sub>0.2</sub>/Si superlattice films for heat flow parallel to thin films
- Using the 300 technique over a range of frequency
  - (1) Low frequency  $\rightarrow$  large thermal diffusion length  $\rightarrow$  for film and substrate  $\kappa$
  - (2) Higher frequency  $\rightarrow$  smaller thermal diffusion length  $\rightarrow$  for film  $\kappa$ , alone

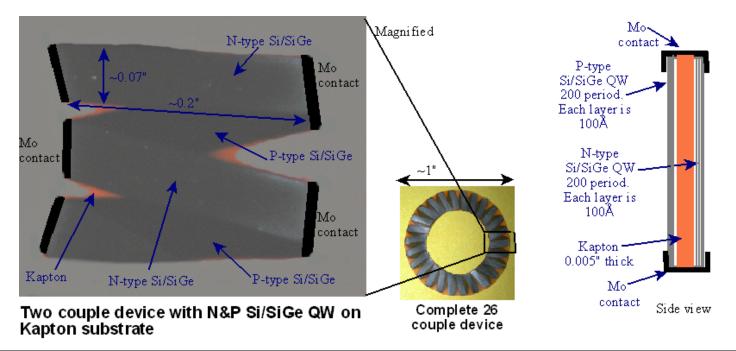
Film Thickness	$\kappa^{in-phase}$		
	W/mK		
0.4μm	~4.6		
1.0μm	4.3		
5.6μm	3.5		

Samples courtesy Hi-Z Inc.

- •Bulk Si K =150 W/mK, and bulk SiGe K =70W/mK
- •Experimental thin film data in agreement with analysis indicating large reduction in thermal conductivity compared to bulk materials
  - To be presented at the MRS Spring meeting, San Francisco, April, 2009

#### Other Experimental Results at Hi-Z:

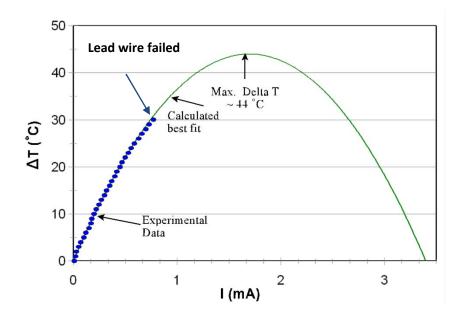
QW Module Performance Verified in a 2-Couple Test With Molybdenum Contacts Having Small Contact Resistance; Comparison with Bulk Module



		Experimental	Calculated 26 Couple Module at ①T = 40 <i>™</i> C		
T <sub>Cold</sub> = 26 ♥ C T <sub>Hot</sub> = 66 ♥ C	2 QW Couples Measured at ①T= 40 ℃  2 QW Couples Measurements Extrapolated to 26 Couple Module at ①T = 40 ℃C		QW With ZT ~3.0	Bulk (Bi,Sb) <sub>2</sub> Se,Te) <sub>3</sub> With ZT ~0.75	
Voltage (V <sub>OC</sub> )	225 mV	2.93 V	3V	0.5V	
Power	0.371 mW	4.82 mW	5 mW	1.5 mW	

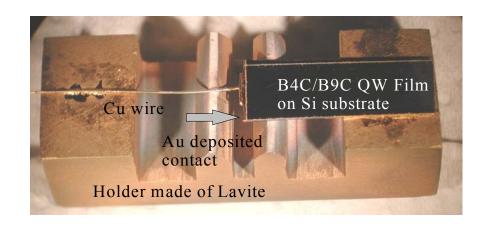
### Other Experimental Results at Hi-Z: Quantum Well Film ZT From Cooling Test Data

# Current Test with P-Type Si/SiGe QW Element



Max.  $\Delta T \approx 44^{\circ}C$ ZT  $\approx 3.5$  @ T  $\approx 25^{\circ}C$ 

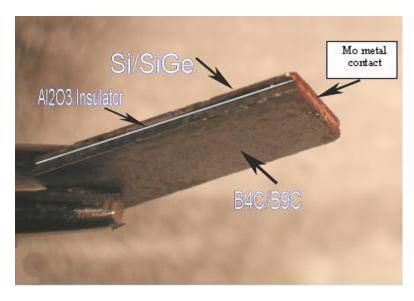
Previous Test with P-Type  $B_4C/B_9C$  QW Element



Max.  $\Delta T = 45$  °C ZT>3 @ T ≈ 25 °C

### Molybdenum Contacted QW Couple

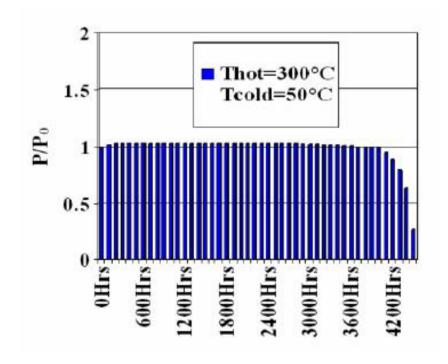




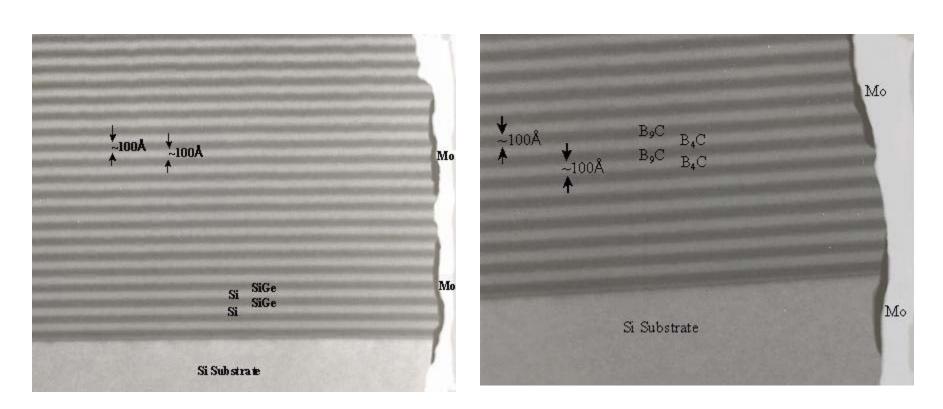
Thermoelectric properties of QW couple with Mo contact compared to calculated values

Room temperature properties	As Fabricated	Calculated
Couple Resistance	1.23 κΩ	1.25κΩ
Couple Voltage output @ ΔT ~ 5°C	9.56 mV	9.60 mV

### **Life Test Data**

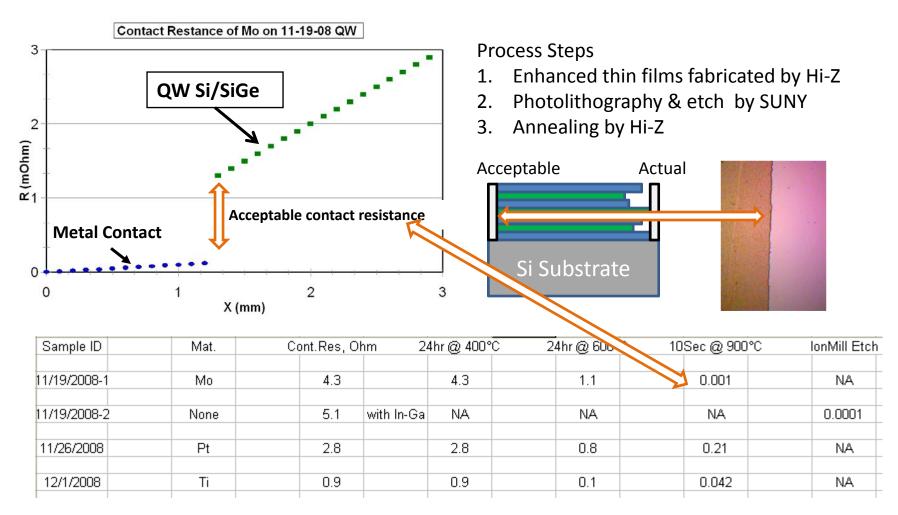


### 150 kX SEM of Si/SiGe Leg of the ~4000 Hours Aged Couple



N and P couple failed due to thermal expansion differences between Mo and QW Materials

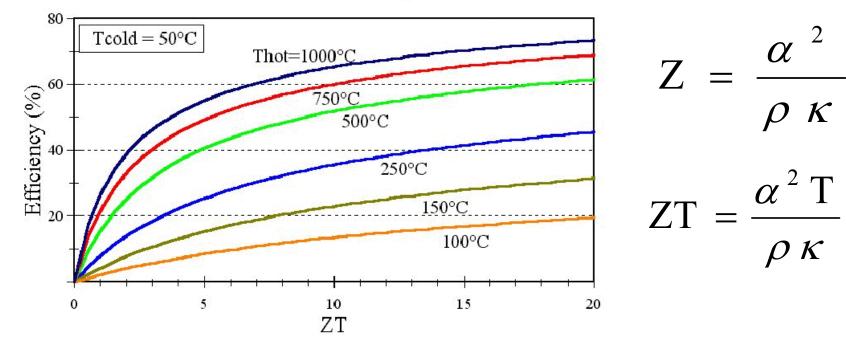
# Electrical contact resistance reduced with photolithography, etch and annealing



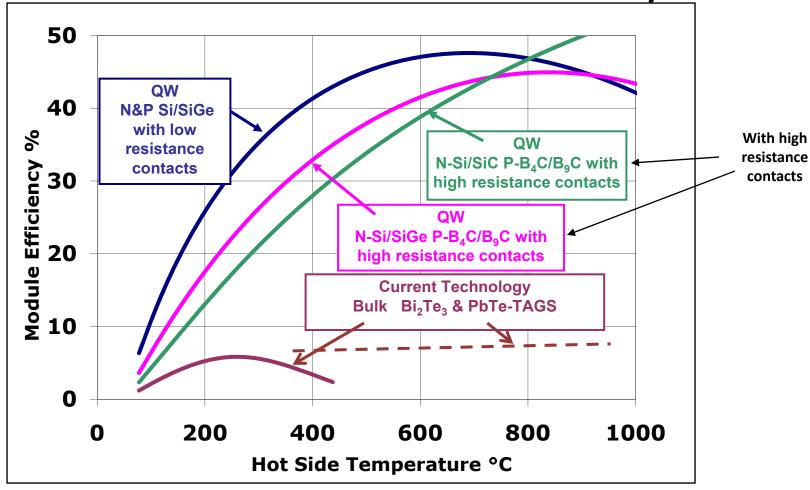
### Thermoelectric Efficiency

Efficiency = 
$$\frac{T_H - T_C}{T_H}$$
  $x$   $\frac{M-1}{M+\frac{T_C}{T_H}}$   $M = \sqrt{1+\frac{1}{2}Z(T_C+T_H)}$ 

Theoretical Efficiency Vs ZT



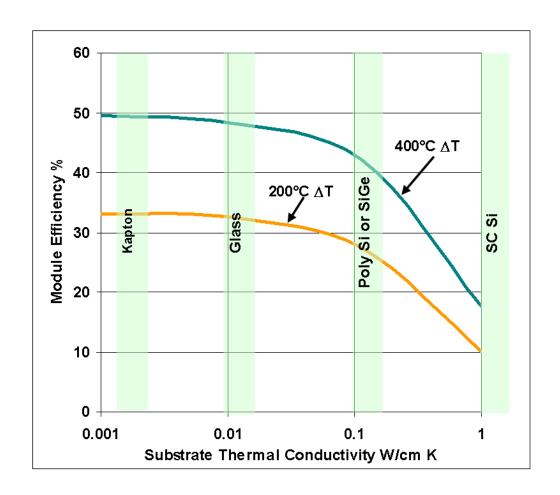
### Predicted QW TE Efficiency

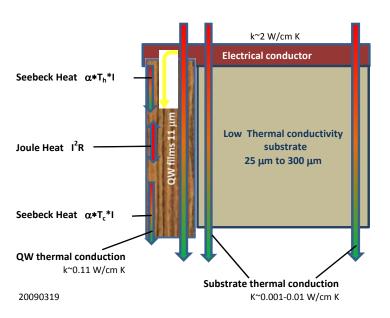


Performance should exceed Si/SiGe with lower resistance contacts.

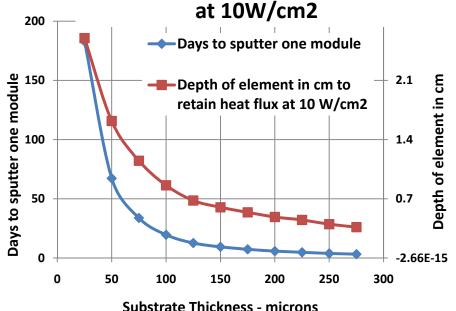
#### Potential Si/SiGe QW TE Module Efficiency with Various Substrates

- Efficiency is strongly dependent on substrate thermal conductivity
- Best QW properties obtained on Single Crystal (SC) Si
- Predicted QW efficiencies for 0.051 mm (0.002 in.) substrate using recent NIST (3/07) and UCSD (12/06) measured QW properties





### 50 Watt QW Module with Heat Flux at 10W/cm2



Reduced production time for enhanced thin films possible with heat flux concentration

Hi-Z's large sputtering machine operating 21 hours/day

Film thickness = 11  $\mu$ m

Sputtering rate = 5 nm/min

### Predicted Efficiency of Enhanced Thin Film Thermoelectrics

QW TE Efficiency > Current Engines at Lower Temperatures

#### **QW TE Generator**

- Cold side = 50°C
- N-type Si/SiC
- P-type B<sub>4</sub>C/B<sub>9</sub>C
- Single QW TE
   Material per Leg &
   Not Segmented

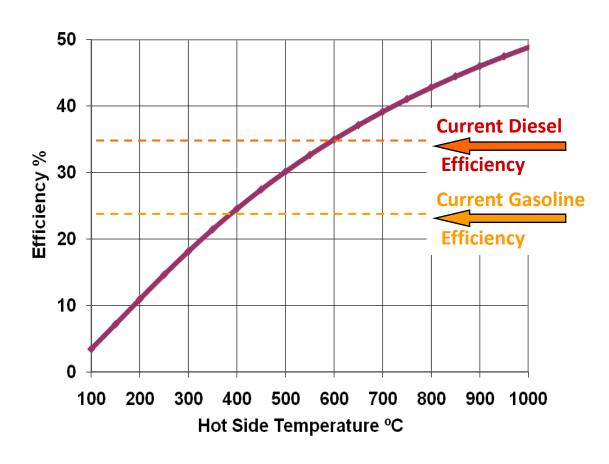
#### Multi-fuel combustor

- Reduced emissions

### No Gasoline /Diesel Engine

 Adiabatic flame temperatures
 ~2000°C or >>higher than multi-fuel combustor

(Drive cycle not included)



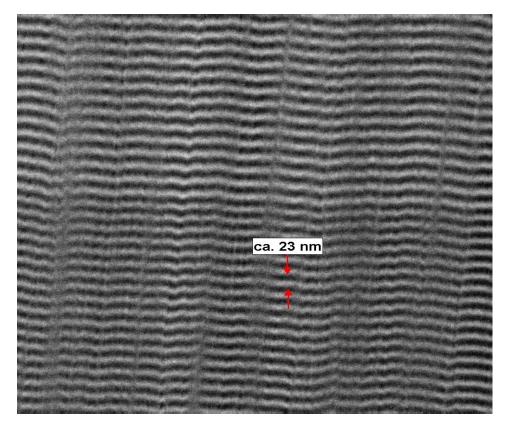
Large area (5 ft²) Sputtering of SiGe Quantum Well Thermoelectrics on Kapton at the General Atomics Production Facility

Thin film deposition on both sides of Kapton produces uniform thickness



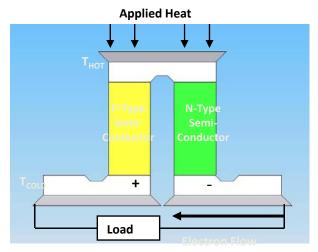
Slight waving of layers is caused at the interfaces due to the large difference between the atom size of Si and Ge

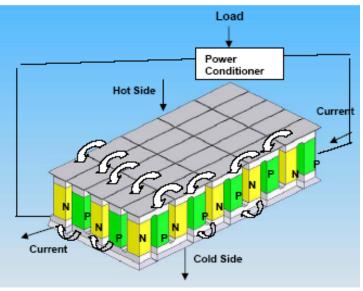
# TEM Thin Films on Si Substrate Sample was coated along with Kapton Film in large Scale Coating Facility at General Atomics



The 23 nanometers includes both a Si and a SiGe layer

# Module Fabrication with Bulk Materials & Enhanced Thin Films V (Quantum Wells)

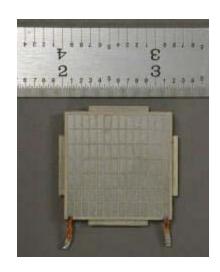




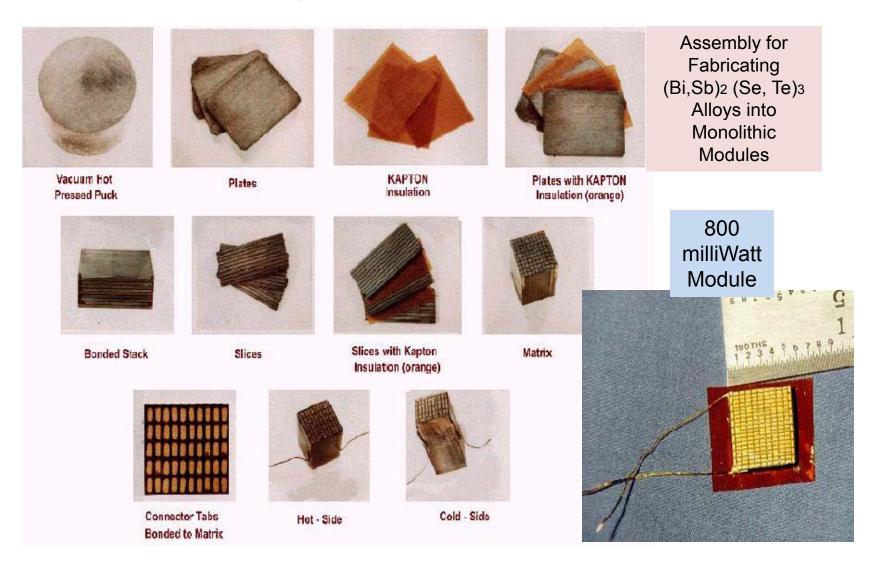
- Thermoelectrics generate power with no moving parts
- Present bulk material technology:
   5% efficient
- Quantum Well nanotechnology will be several times more efficient

#### **One Current Product**

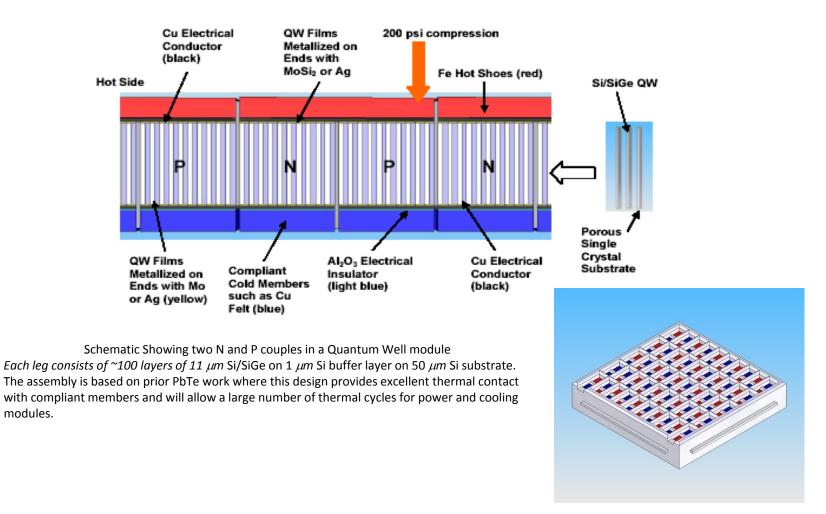
HZ-2 Watt Commercial Module



## Bulk Alloy Milli-Watt Modules



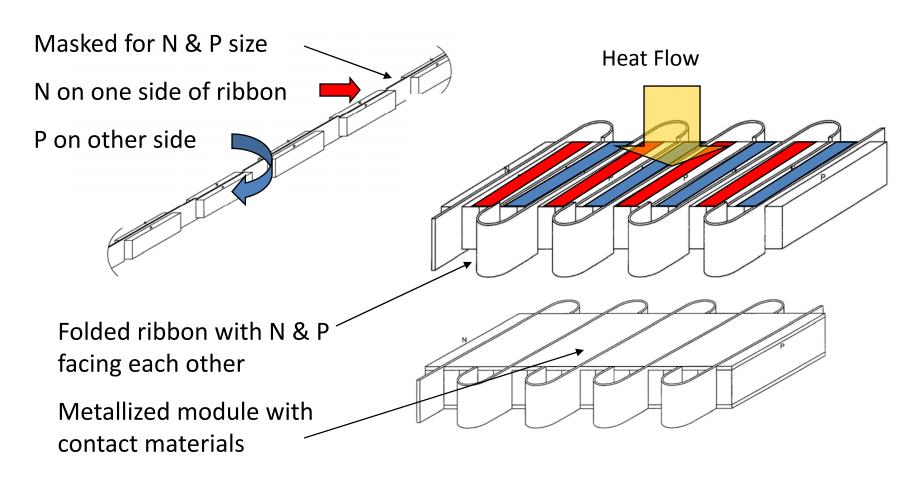
### Schematic Showing two N and P Couples in a Quantum Well Module



modules.

### Process Change - Folded Quantum Well Module

Sputtering process forms module & eliminates eggcrate Improves efficiency and reduces costs



#### **Stacked Thermoelectric Module**

• A stacked module consists of P legs, N legs, spacers and a clamp.

• Contacts are deposited on the top and bottom of the legs and on one side of the spacer.

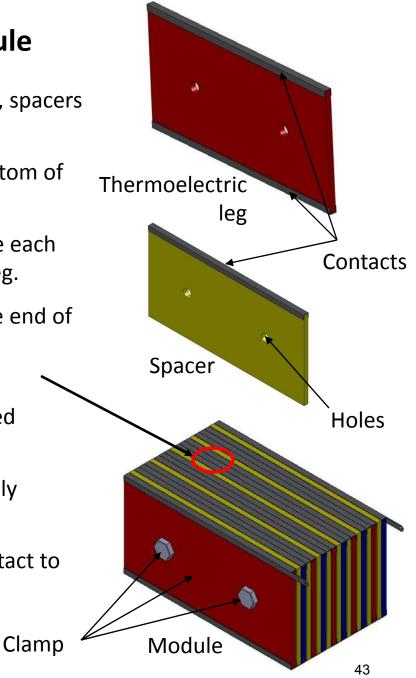
• Alternating N and P legs are stacked beside each other and a spacer is placed between each leg.

 The contact on the spacer will connect one end of the P leg to the adjacent end of the N leg.

• By alternating the side that the contact is positioned on, all of the legs can be connected electrically in series.

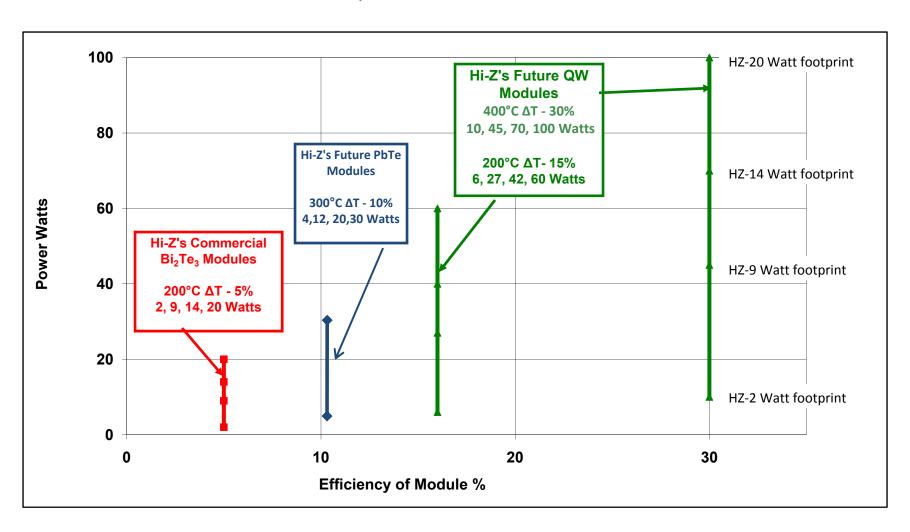
 Holes will allow alignment pins to accurately position each leg/spacer.

• A clamp will hold the stack-up in close contact to ensure good electrical continuity.



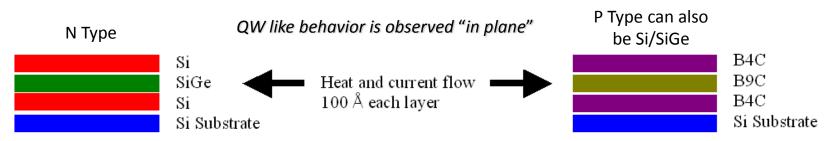
### Forecasted Thermoelectric Progress

Module footprints from HZ-2 to HZ-20 sizes



#### Summary and Future Direction

- Alternating 100 Å (10 nm) thick layers of N type Si/SiGe and P type B<sub>4</sub>C/B<sub>9</sub>C were deposited on 5 μm thick Si substrates:v
  - 14% efficiency was measured at a T<sub>H</sub> of 250°C and T<sub>C</sub> of 50°C
  - Si/SiGe or Si/SiC can also be used as the P type leg.



- -Encouraging Seebeck coefficient  $\alpha$  (1,000 $\mu$ V/°C) and  $\rho$  resistivity (1millohm–cm) data has been observed by 4 groups besides Hi-Z
- -Measurements by UCSD show the thermal conductivity values are  $\frac{1}{3}$  to  $\frac{1}{2}$  of bulk properties which are in agreement with theoretical models
- -A new test device developed at Hi-Z, indicates ZT values of ~5 with Si/SiGe alternating layers
- 2. Good thermal and thermoelectric stability exhibited thus far:
  - In isothermal testing at 600°C, 400 hours and 1000°C, 24 hours
  - Output of a N and P couple at T<sub>H</sub> of 300°C and T<sub>C</sub> of 50°C remained stable for 4000 hours
  - Many more couples to be life tested
- 3. Joining the QW materials with Mo shows promise. Appears contact resistance can be reduced to low levels. Subcontract with SUNY Albany nano fabrication facility allows us to take advantage of their on going development in this area.

### Summary and Future Direction Continued

- 4. Large area deposition:
  - Sputter QW film onto 6 inch area diameter Si wafers is planned
  - Major coating facility demonstrated multiple layers of Si/SiGe 10 nano meter thick can be deposited over large area. (Several square feet) of Kapton
  - Evaluations of films and further scale up to planned
- 5. Lower thermal conductivity substrates being pursued with SUNY Albany via several techniques. Kapton and glass may also be suitable as a substrate
- 6. Several module designs identified and low cost modeling studies indicates ~ \$0.50 /Watt is achievable. Module fabrication is planned
- 7. Large increases in thermoelectric conversion efficiency (>3 times) appear feasible from  $T_H$ 's of 150°C to 1000°C.
- 8. With higher efficiencies waste heat recovery markets become economical. Today they are marginal. Plan underway to work with several large companies
- There are many marketing opportunities for this encouraging QW Technology. Several are multi billion dollar in size
- 10. Future work oriented towards fabricating couples and modules as well as material optimization.